Atmospheric Reactivity Research on Selected Pesticides

William P. L. Carter
CE-CERT, University of California, Riverside
August 28, 2007

Outline

- Types of pesticide VOCs of interest for reactivity research
- UCR pesticide reactivity research project: objectives, methods, and results
- Estimated relative O_3 and PM impacts of pesticide VOCs
- Conclusions

UCR Project to Investigate Atmospheric Reactivities of Selected Pesticide VOCs

Background

- Data are not available concerning O_3 and PM impacts for many types of pesticide VOCs used in California. Therefore, estimates of these impacts are very uncertain

Objectives

- Reduce uncertainties in estimates of O_3 impacts for pesticides used in California
- Obtain qualitative information on relative PM impacts or representative pesticide VOCs
- Make recommendations on how to represent pesticide VOCs in airshed models

Approach

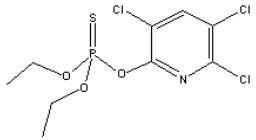
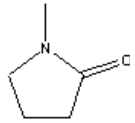
- Assess available information and select representative pesticide-related compounds most in need of study
- Conduct environmental chamber experiments to develop mechanisms for predicting O_3 impacts of the studied compounds
- Incorporate mechanisms for these and related compounds into the overall mechanism used to predict ozone impacts of VOCs.
- Derive ozone impacts of the pesticides in various O_3 reactivity scales, including the MIR scale used in California regulations
- Obtain data on relative PM impacts of the studied compounds, and compare them with other compounds studied previously

Volatile Compounds in Pesticide Profile in 2000 California VOC Emissions Inventory

Compound	Wt. %	Structure	Comments
Methyl Bromide	25%	CH_3Br	Very low reaction rate
Methyl Isothiocyanate	18%	CH_3NCS	No mechanism. Reaction rate known
1,3-Dichloropropenes	11%	$ClCH=CHCH_2Cl$	Some mechanistic data available
Chloropicrin	9%	CCl_3NO_2	Previously studied
Aromatic 200 Solvent	5%	Aromatic Mixture	Accuracy of existing mechanism uncertain
Xylene Solvent	5%	xylene isomers	Previously studied
Various Thiocarbamates	~4%	Compounds with >NC(O)S- group	Some kinetic and mechanistic data available

Volatile Compounds in Pesticide Profile in 2000 California VOC Emissions Inventory

(continued)

Compound	Wt. %	Structure	Comments
Kerosene	2%	Hydrocarbon mixture	Some data on lighter mixtures
Chlorpyrifos	2%		Volatility too low to study (vp ~30 ppt)
Methy isobutyl ketone	1%	$CH_3C(O)CH_2CH(CH_3)CH_3$	Previously studied
Acrolein	0.7%	CH_2=CHCHO	Previously studied
Glycerine	0.5%	$HOCH_2CH(OH)CH_2OH$	Mechanism can be estimated
Propylene Glycol	0.5%	$CH_3CH(OH)CH_2OH$	Previously studied
N-methyl pyrrolidinone	0.5%		Previously studied

Pesticide Related VOCs Chosen for Study

Methyl Isothiocyanate

- Highest emissions in profile with non-negligible reaction rate.
- No mechanisms have been derived or evaluated for isothiocyanates.

1,3-Dichloropropenes

- 2nd highest in profile with non-negligible reaction rate.
- Mechanisms of halogenated compounds are uncertain

EPTC (S-ethyl N,N-di-n-propyl thiocarbamate)

- Chosen as a representative thiocarbamate.
- Some kinetic and mechanistic data available, but no data to evaluate mechanisms for thiocarbamates

continued ...

Pesticide Related VOCs Chosen for Study
(continued)

Kerosene

- Highest emissions in profile of hydrocarbon solvents
- Complex mixture of C_8-C_{18} alkanes (82%) and aromatics (18%)
- Data available to test mechanisms for “mineral spirits” and other hydrocarbon solvents used in coatings, but not kerosene.
- Mechanism derived based on speciation data provided by ExxonMobil Process Laboratories in Baton Rouge, LA

Carbon Disulfide (CS_2)

- Known to be important as a pesticide breakdown product
- Kinetic and mechanistic data available, but no data available to evaluate mechanisms for ozone and PM impacts.

Environmental Chamber Experiments

Purpose

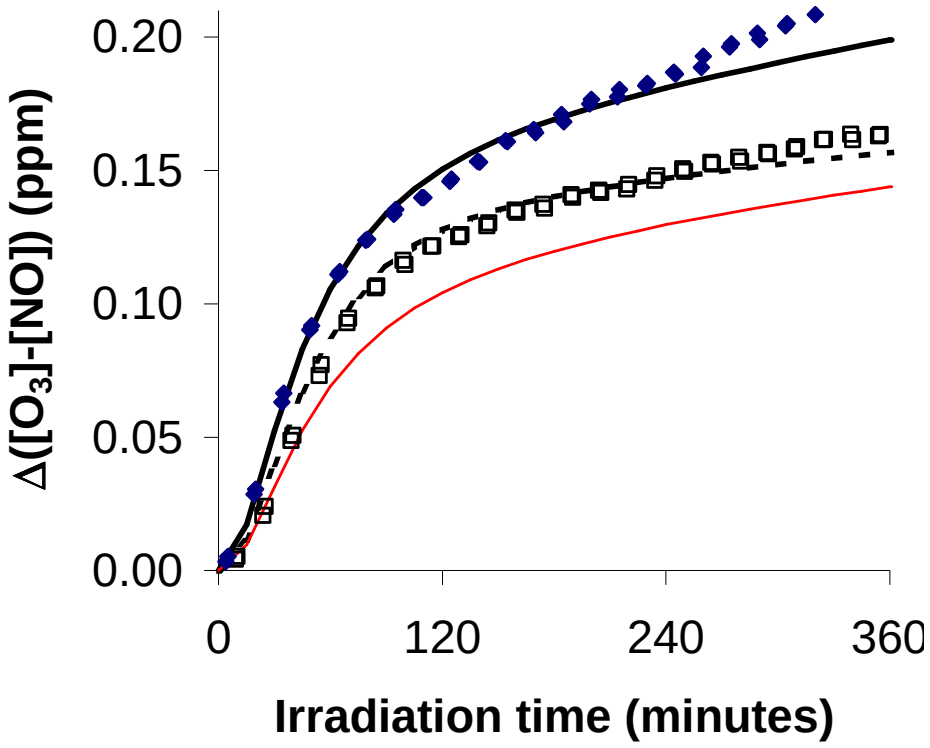
- Provide data to test ability of mechanisms to predict O_3 impacts
- Obtain qualitative information on relative PM impacts
- Obtain data on relevant VOC rate constants, where needed

Types of Experiments

- Incremental reactivity experiments: Add test compound to reactive organic gas (ROG) surrogate - NO_x irradiations simulating ambient conditions
- Single VOC - NO_x irradiations where useful
- UCR EPA chamber (with blacklight light source) employed

Results of Selected Experiments

EPA589: Surrogate + MITC

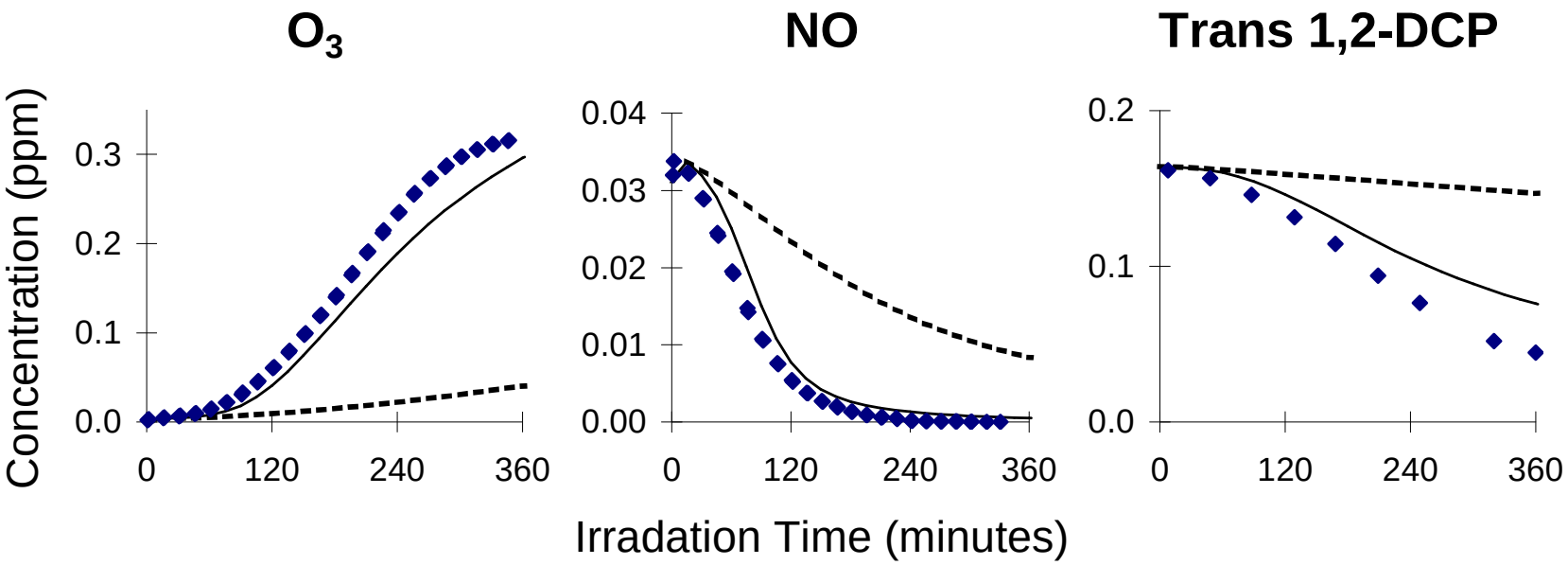


- Base Experiment (25 ppb NOx, 1 ppmC ROG surrogate)
- Model simulation of Base Case Experiment
- Experiment with 1 ppm MITC added
- Model simulation of test experiment (Mechanism "A")
- Model simulation of test experiment (Mechanism "B")

- **Mechanism A: Major fate of HSO in experiment is HSO + O_2**
- **Mechanism B: Major fate of HSO in experiment is HSO + NO_2**

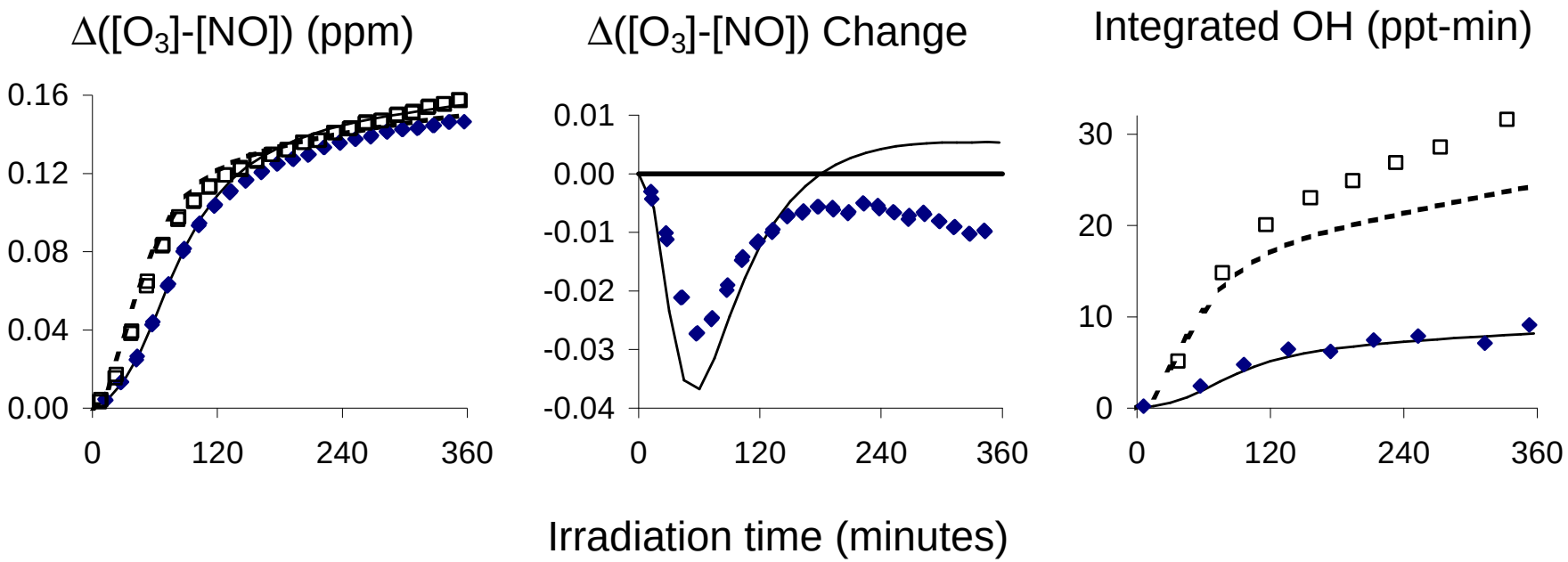
Results of Selected Experiments (continued)

EPA551B: 0.4 ppm 1,3-Dichloropropenes + 50 ppb NOx



Results of Selected Experiments (continued)

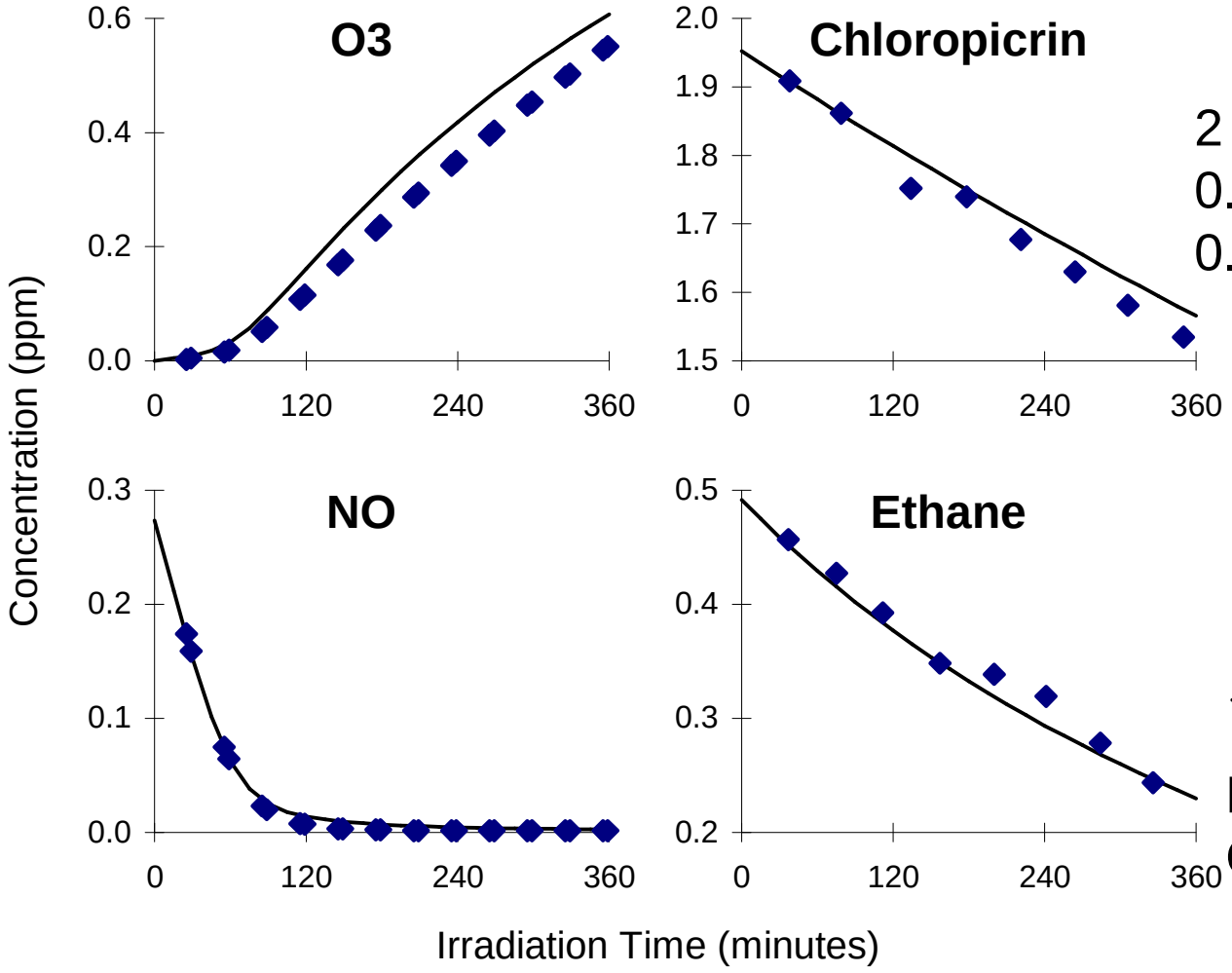
EPA590: Surrogate + EPTC



- ▫ Base Experiment (25 ppb NOx, 1 ppmC ROG surrogate)
- - - Model simulation of base experiment
- ◆ Experiment with 0.25 ppm EPTC added
- —— Model simulation of added EPTC experiment

Results of Selected Chloropicrin Experiment

(Carried out for a previous project)



CTC134A

2 ppm Chloropicrin
0.4 ppm NOx
0.5 ppm ethane

◆ Experimental

— Model

Ethane is tracer for Cl atom formation

Mechanism Development Results

Mechanisms were derived for MITC, EPTC, and CS_2 that were consistent with the chamber results

- Data used to obtain rate constants for OH + MITC and to refine the rate constant for OH + EPTC
- Uncertain aspects of mechanisms for MITC, EPTC, and CS_2 had to be adjusted to satisfactorily simulate the chamber data
- Mechanism derived for EPTC were used to derive estimated mechanisms for molinate, pebulate, and thiobencarb,

The model for Kerosene based on analysis by ExxonMobil gave satisfactory simulation of the chamber results

continued ...

Mechanism Development Results (continued)

Mechanisms were derived for the 1,3-dichloropropenes and chloropicrin that were consistent with chamber results

- Chlorine chemistry was added to the SAPRC-99 mechanisms to permit representation of these chlorine-containing compounds
- It is necessary to explicitly represent chloroacetaldehyde to correctly simulate dichloropropene reactivity. This has implications for mechanisms for chlorinated VOCs in general.
- An updated mechanism for chloropicrin developed and found to give good simulations of experiments carried out previously.

The mechanisms developed for these pesticide compounds are being incorporated in the updated SAPRC-07 mechanism that is nearing completion

Representative MIR and EBIR Reactivities

Compound or Mixture	O_3 Reactivity (Mass Basis)	
	MIR	EBIR
Ambient Emissions Mixture	3.6	0.8
1,3-Dichloropropenes	4.3	0.9
Chloropicrin	1.9	1.2
EPTC	1.6	0.5
Kerosene	1.5	0.3
MITC	0.3	0.2
Ethane *	0.3	0.13
Carbon Disulfide	0.2	0.13
Methyl Bromide	0.02	0.01

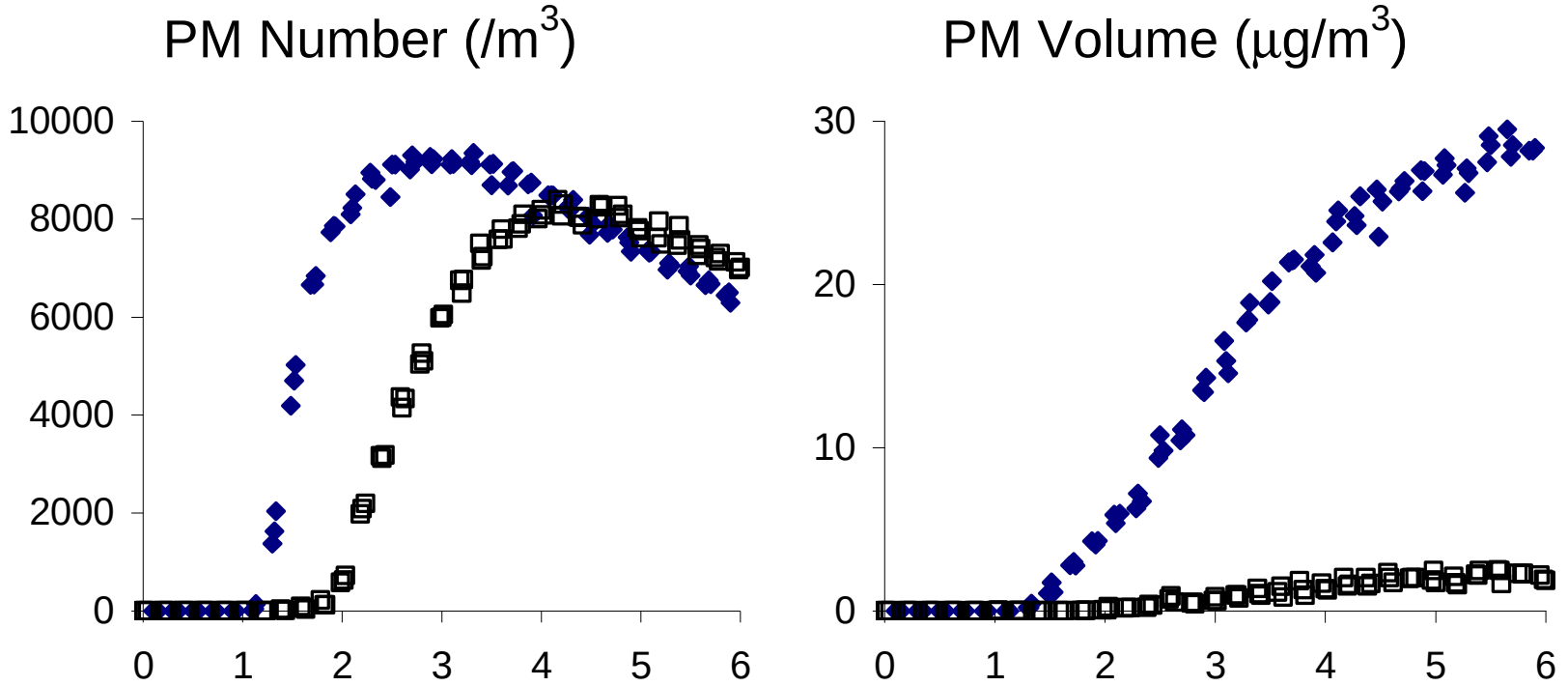
Calculated using new SAPRC-07 Mechanism

* Used by the EPA as the standard to define “negligible” reactivity

PM Measurements in the UCR EPA Chamber

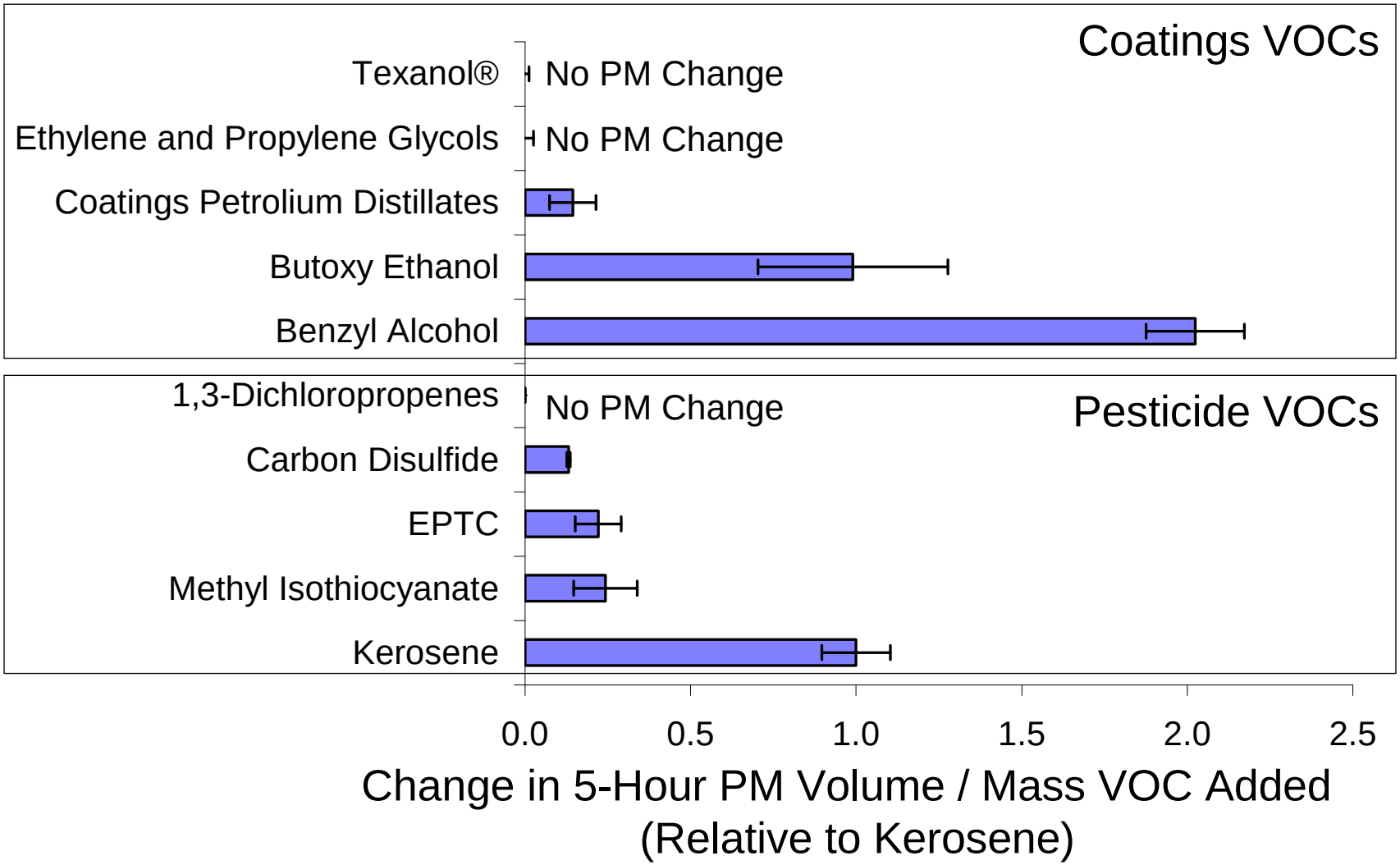
- PM Measurements are being made in conjunction with most UCR EPA chamber experiments. PM alternately sampled from each of the two reactors, switching every 10 minutes
- Number densities of particles in 71 size ranges (28 - 730 nm) measured using a a Scanning Electrical Mobility Spectrometer. Data used to compute particle number and volume densities
- Background PM formation now less than 0.5 $\mu g/m^3$. (Was up to 2 $\mu g/m^3$ in Reactor A before it was replaced)
- Most experiments to date are unhumidified with no seed aerosol
- PM measurements made during reactivity experiments with representative architectural coatings and pesticide VOCs.

Representative PM Data



- Base Experiment (30 ppb NOx, 0.6 ppmC Base ROG)
- 1.5 ppmC Kerosene Added

Relative PM Formation In Surrogate - NOx + Test VOC Experiments



Conclusions

- Uncertainties in estimates of O_3 impacts of important types of pesticides used in California have been reduced
- Information has been obtained to improve O_3 impact estimates for Sulfur- and Chlorine-containing compounds in general
- Pesticide reactivities have been added to reactivity scales that can be used for regulatory applications
- Information has been obtained concerning differences in PM impacts of representative pesticides
- Uncertainties remain in mechanisms for many types of VOCs
- Improved mechanisms and data are needed to *quantitatively* predict PM impacts in models
- Air quality impacts of very low volatility pesticides are uncertain

Acknowledgements

- **Irina Malkina, Kurt Bumiller, Bethany Warren**
  - Major effort in conducting pesticide chamber experiments
- **David Cocker**
  - Overall guidance for PM studies
- **Dennis Fitz, Kurt Bumiller, Claudia Sauer, John Pisano, Charles Bufalino, Matthew Smith**
  - Assistance in design and construction of UCR EPA Chamber
- **California Air Resources Board**
  - Funding source for pesticide reactivity and mechanism development projects
- **United States Environmental Protection Agency and South Coast Air Quality Management District**
  - Funding sources for chamber construction and for PM studies on coatings VOCs, respectively